

Effects of monomer composition on the swelling of core-shell copolymers with high content of carboxylic groups

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Abstract : The swelling properties of a series of core-shell copolymers, prepared by two-stage emulsion polymerization, based on different monomer compositions and with a carboxylic acid-rich core have been studied at room temperature. Swelling is highly dependent on pH, monomer composition, and the monomer type in the shell. Generally, the average particle size of the core-shell copolymers remains more or less the same within the pH range from 4 to 7. However, the particle size has increased significant in alkaline medium and reached a maximum at pH 10. Increasing the proportion of styrene to butyl acrylate or methyl methacrylate generally reduces the extent of swelling, presumably due to the lower hydrophilicity of styrene over butyl acrylate or methyl methacrylate.

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Introduction

There has been considerable interest in the studies on core-shell latex particles with many research papers and reviews being published from time to time [1-14]. Lee et al.[3] have found that the morphology of core-shell latex particles polymerized with hydrophobic shell monomers (polymer II) in the presence of hydrophilic core polymer particles (polymer I) was dependent on the hydrophilicity and molecular weight of the core polymer and the extent of phase separation between the two polymers involved. The extent of phase separation in the two-stage latex particles is expected to increase with greater incompatibility between the core and shell polymers.

The properties of latex particles containing lightly cross-linked polymer gel bearing weakly acidic or weakly basic pendant groups change in respond to the changes in pH and ionic composition of the aqueous medium. When the gel is relatively hydrophilic and contains acidic pendant groups, the swelling increases as solution pH increases. On the other hand, a weakly basic hydrophilic gel could swell as the solution pH decreases. The polyelectrolyte gel remains in a collapsed state until the external solvent reaches a critical pH, at which point the gel abruptly increases its equilibrium swelling [15-17]. This can be demonstrated by plotting the gel volume versus pH. The transition in gel volume can also be induced by varying the ionic composition [18], temperature [19-21] or solvent composition [16, 20, 22]. This has stimulated research on the feasibility of applications of such gels as artificial muscles or switches, components in chemical separation systems [23], and as

physiologically sensitive drug delivery devices [17, 21, 24].

Kong et al. [14] have prepared monodisperse latex particles with a core-shell morphology via seeded emulsion polymerization, and used alkali and acid treatment to generate pores in the particles. Okubo et al. [25, 26] have also reported an alkali treatment method on their carboxylic acid-containing copolymer latexes to produce pores in the polymer particles.

In this study, core-shell latex particles containing carboxylic acid groups were produced via seeded emulsion polymerization. The seed latex (first-stage hydrophilic, polymer I) contained 19.5 mol % of methacrylic acid in the monomer mixture. The monomer mixture used in the second stage (polymer II) contained a fixed 4 mol % of carboxylic acid with different mole ratio of styrene/BA or styrene/MMA. The purpose was to investigate the effects of monomer composition in shell polymer II on the swelling of latex particles at various pH and the swelling of resulting polymer film in NaOH solution.

Experimental

Materials

Butyl acrylate (BA, >99%, Fluka), methyl methacrylate (MMA, >99%, BDH), styrene (St, >99%, R & M), 2-hydroxyethyl methacrylate (2HEMA, 97%, Aldrich), methacrylic acid (MAA, >99%, Merck-Schuchardt) and acrylic acid (AA, >99%, Fluka) were used without further purification. Potassium persulfate (97%) from Avocado Research Chemicals was used as the polymerization initiator. The polymerization emulsifiers were sodium lauryl

sulfate and NP-40, which is nonyl phenol ethoxylate with 40 units of ethylene oxide.

Preparation of latex samples

The emulsion polymerization was carried out in a glass reactor flask and the stirrer speed was controlled between 200-500 rpm. The mode of emulsion polymerization was a semi-continuous process and reactions were carried out at 75°C.

The seed latex was prepared according to the recipe of Polymer I (which served as the core), and the core-shell polymer was prepared by seeded

emulsion polymerization according to the recipe of Polymer II in Table 1. The composition of Polymer II shown in Table 1 was the actual recipe of CS5 in Table 2(b). The styrene/MMA or styrene/BA mole ratios was altered according to Tables 2(a) and 2(b) by keeping the respective total weight of styrene and MMA or styrene and BA constant. For comparison purposes, latexes with similar compositions of Polymer II without the hydrophilic seed latex were also prepared; these are CC1, CC2 and CC3 in table 2(a). All latexes were prepared in acidic pH.

Table 1 : The recipes (by weight) of seeded emulsion polymerization.

Polymer	I	II
Ingredient	Quantity (g)	Quantity (g)
Distilled water	560.0	490.0
NP40 ^a	0.7	3.2
Sodium lauryl sulfate	3.5	3.5
Potassium persulfate	1.2	1.0
Seed latex (Polymer I)	-	87.5
Styrene	-	55.1
Methyl Methacrylate	35.0	3.7
Butyl acrylate	84.0	53.9
Methacrylic acid	21.0	2.5
Acrylic acid	-	1.2
2-Hydroxyl ethyl methacrylate	-	6.1
Total charge	705.4	707.7

^a Nonyl phenol ethoxylate (40 units of ethylene oxide)

The composition of polymer II in this table corresponds to CS5.

Table 2(a) : Latex samples with different Styrene/MMA mole ratio.

Sample Code^b	Styrene/MMA mole ratio
CC1	1.65/1
CC2	3.61/1
CC3	17.33/1
CS1	1.65/1
CS2	3.61/1
CS3	17.20/1

^b CC refers to conventional copolymer; CS refers to core-shell copolymer.

The amount of BA was kept constant at 30 mol% of the monomer mixture.

Table 2(b) : Latex samples with different Styrene/BA mole ratio.

Sample Code^b	Styrene/BA mole ratio
CS3	1.94/1
CS4	1.59/1
CS5	1.26/1
CS6	1.04/1
CS7	0.82/1

^b CC refers to conventional copolymer; CS refers to core-shell copolymer.

The amount of MMA was kept constant at 3.4 mol% of the monomer mixture.

Particle size determination

The latex particle diameter was determined by submicron Particle Sizer (Coulter N4 Plus). The latex samples were adjusted to suitable dilution with distilled water and adjusted to different pH, namely pH 4.5, 6, 7.5, 9 and 10.2 with ammonia solution.

Preparation of polymer film

The latex was drawn on smoothen aluminum foil or glass panel with a bar coater (thickness 50 microns). The wet film was dried at 60°C for 1 hour followed by 150°C for 30 minutes.

Swelling of film

The dried film that was coated on aluminum foil was cut into a round shape with a disc cutter with fixed diameter of 20.4 mm (d_0). The film was then soaked in 0.25 M sodium hydroxide solution at room temperature for 30 hours. The diameter of the swollen film was measured (d_1). The swelling is assumed to occur to the same extend in all directions. Percent of swelling of film in volume was calculated as follows:

$$\% \text{ swelling} = \frac{v_1 - v_0}{v_0} \times 100\%$$

$$= [(d_1/d_0)^3 - 1] \times 100\%$$

where v_1 represents the swollen volume, while v_0 the initial volume.

Glass transition temperature (T_g)

Differential Scanning Calorimetry (Perkin Elmer 7 Series Thermal Analysis System) was used to determine the T_g of the polymer film. Each sample was first scanned from 0 to 200°C and then quenched

cooled rapidly at -50°C/min to -55°C. The next heating scan was carried out from -55°C to 150°C at 20°C/min. Each sample was between 10-20 mg, encapsulated in non-volatile aluminum sample pan.

Minimum film-forming temperature (MFT)

The MFT of polymer film was determined by drying the wet emulsion film on glass panel at different temperatures, and noting the lowest temperature at which the polymer film could form.

Results and Discussion**Effect of two-stage polymerization on latex particle diameter**

In comparison to the seed latex (Polymer I) the core-shell latex particles have significantly larger diameters. There was an increase of 40-77% in the particle diameter (Table 3).

The three latexes without the seed latex (CC1, CC2 and CC3) were prepared via conventional emulsion polymerization with the same monomer composition as in latexes CS1, CS2 and CS3 respectively. The average particle diameters of the latex CS1 was 59.8% larger than that of CC1, while latex particle diameter of CS2 was 113% larger than that of CC2, and CS3 was 73.2% larger than CC3.

Effect of pH on latex particle swelling

The results in Table 4 show that the particle diameter of the styrene-acrylate latexes CC1, CC2 and CC3 prepared by conventional emulsion polymerization technique does not swell in alkali pH. By contrast, when a carboxylic acid-rich polymer I was introduced as seed, the core-shell latex particles have swollen significantly in alkali pH (at pH 9 and pH 10.2).

Table 3 : The effect of seeded emulsion polymerization on particle diameter.

Polymer Type	Sample Code	Particle Diameter, nm
Seed latex	Polymer I	74.9
Conventional	CC1	65.6
Conventional	CC2	62.1
Conventional	CC3	64.1
Core-shell	CS1	104.8
Core-shell	CS2	132.5
Core-shell	CS3	111.0
Core-shell	CS4	108.1
Core-shell	CS5	104.7
Core-shell	CS6	107.4
Core-shell	CS7	114.7

Table 4 : The effect of pH on particle swelling.

Sample Code	Mean Particle Diameter /nm					Swelling of Particle ^c , %
	pH 4.5	pH 6.0	pH 7.5	pH 9.0	pH 10.2	
CC1	65.6	66.9	66.9	66.9	64.2	-6.3
CC2	62.1	64.0	67.0	63.0	61.2	-4.3
CC3	64.1	67.7	64.3	64.9	63.6	-2.3
CS1	104.8	106.9	104.8	115.5	166.8	303.2
CS2	132.5	131.8	132.8	167.8	217.3	341.1
CS3	111.0	108.9	110.8	167.0	166.3	236.3

^c Comparing the volume change from pH 4.5 to pH 10.2.

Tg of the resulting dried polymer films

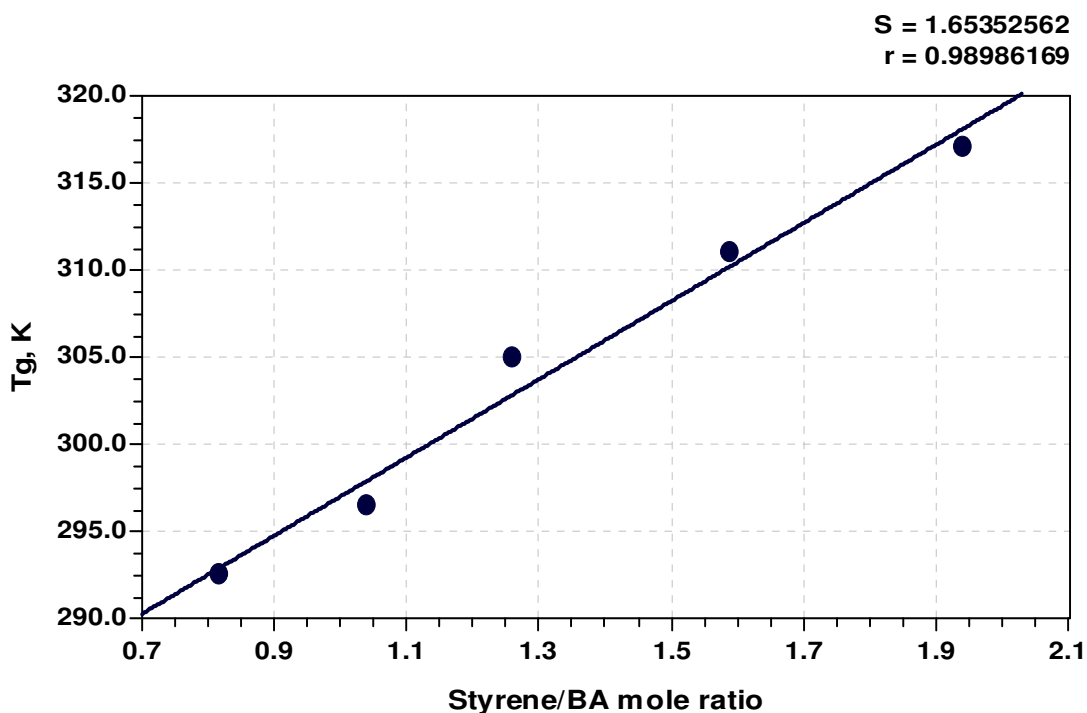
Comparing the homopolymers, polystyrene has a higher Tg than poly(butyl acrylate) [27]. Hence, as the styrene/BA ratio is increased, the Tg of the copolymer would become higher. By linear least square analysis (Figure 1), the correlation of styrene/BA mole ratio in polymer II and the Tg of the resulting film has produced a reasonable linear fit with a correlation coefficient of 0.990.

Figure 2 shows that the extent of swelling of the core-shell latex particles with different styrene/BA ratio is affected by the Tg of the copolymer. When the Tg became lower, the particle was able to swell to higher extent at pH 10. However, the swelling of

latex particles did not exhibit a good linear correlation with the Tg.

Swelling of dry polymer films

Figure 3 shows that the swelling of the polymer film in NaOH solution was inversely proportional to the Tg of the polymer with different styrene/BA ratio. The graph obtained has an approximate linear fit with correlation coefficient of 0.952. The above results suggest that it is feasible to produce polymer film with the required extent of swelling via the two-stage emulsion polymerization technique. Hence, by varying the styrene/BA ratio in polymer II in the presence of the carboxylic acid-rich seed, the Tg as well as the extent of swelling of the polymer film can be predicted.

**Figure 1** : The effect of styrene/butyl acrylate mole ratio in polymer II on the Tg of the core-shell polymer.

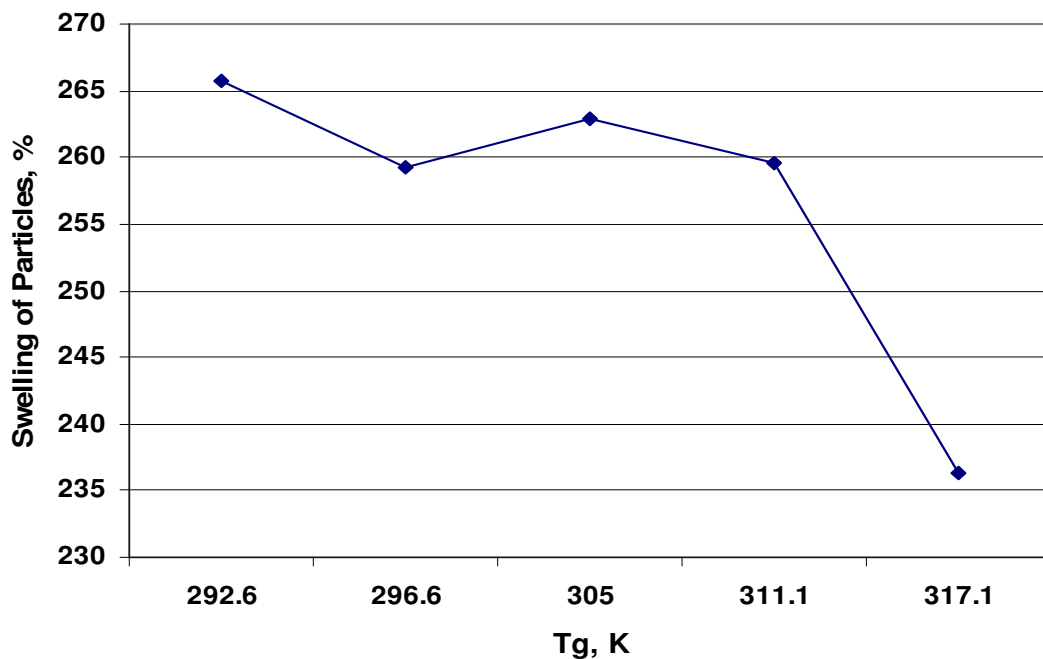


Figure 2 : The effect of polymer Tg with different styrene/butyl acrylate mole ratio in polymer II on the extent of swelling of latex particles of the core-shell copolymer.

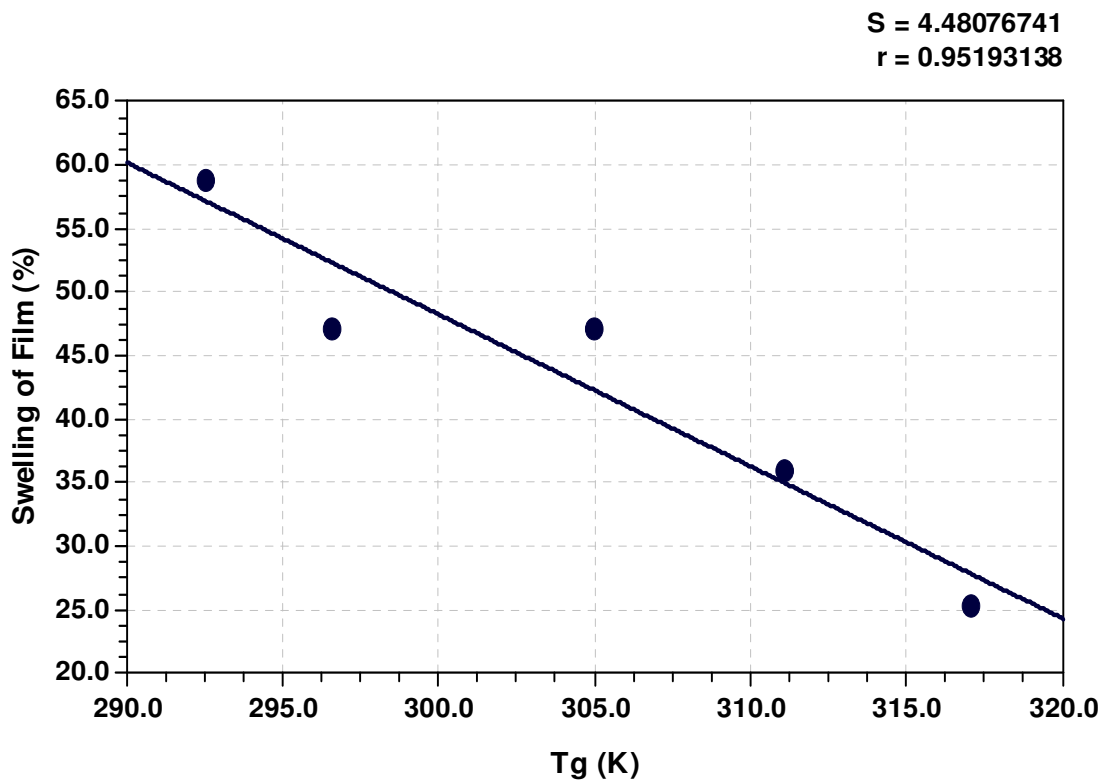


Figure 3 : The effect of polymer Tg with different styrene/butyl acrylate mole ratio in polymer II on the extent of swelling of the core-shell copolymer film.

Styrene/MMA ratio on the swelling of core-shell latex particles and polymer film

The extent of swelling of the latex particles as well as the polymer films of the core-shell copolymer (CS1, CS2 and CS3) latexes were affected by the styrene/MMA ratio (Tables 5 and 6). When styrene/MMA was high, the extent of swelling became less. Both polystyrene and PMMA have T_g fairly close to each other [27], hence, as the styrene/MMA ratio is varied, the T_g of the copolymer remain more or less the same (Table 7).

Presumably the styrene unit is more rigid and less stretchable than MMA unit. In addition, the much lower solubility of styrene in water than MMA [28], must have affected the volume transition as well, hence, resulted in less swelling of the copolymer latex particles with higher styrene/MMA ratio.

The effect of styrene/MMA ratio on the swelling of the dry polymer film in NaOH solution was not significant in the conventional copolymer samples CC1, CC2 and CC3 (Table 6). The slight swelling was presumably due to the presence of four mole percent of carboxylic acid in the polymer system.

Effect of the presence of carboxylic acid-rich seed on the hardness of polymer film

The results in Table 7 show that polymer films of the core-shell copolymers (CS1, CS2 and CS3) have lower MFTs than the conventional copolymer films (CC1, CC2 and CC3) due to the presence of the hydrophilic carboxylic acid-rich core (polymer I), which tend to retain water.

Conclusions

The study on the effects of monomer composition on the swelling of core-shell copolymers with 19.5 mol % of methacrylic acid in the seed latex was carried out on both the latex particles and the polymer film. Our results have shown that the extent of phase transition in volume of such a system depends on the type of monomer and composition in polymer II. Increasing the proportion of styrene to butyl acrylate or to methyl methacrylate generally reduces the extent of swelling. Swelling is highly sensitive to pH change due to the presence of high content of carboxylic acid in the polymer system.

Table 5 : The effect of styrene/methyl methacrylate mole ratio in polymer II on the swelling of latex particles.

Sample Code	Styrene/MMA mole ratio	Swelling of Particle ^c , %	Sample Code	Styrene/MMA mole ratio	Swelling of Particle ^c , %
CC1	1.65/1	-6.3	CS1	1.65/1	303.2
CC2	3.61/1	-4.3	CS2	3.61/1	341.1
CC3	17.33/1	-2.3	CS3	17.20/1	236.3

^c Comparing the volume change from pH 4.5 to pH 10.2.

Table 6 : Effect of styrene/methyl methacrylate mole ratio in polymer II on the swelling of polymer film.

Sample Code	Styrene/MMA mole ratio	Swelling of Film ^d , %	Sample Code	Styrene/MMA mole ratio	Swelling of Film ^d , %
CC1	1.65/1	13.8	CS1	1.65/1	43.3
CC2	3.61/1	9.1	CS2	3.61/1	37.8
CC3	17.33/1	10.7	CS3	17.20/1	25.4

^d After soaking in 0.25 M NaOH for 30 hours.

Table 7 : T_g and MFT of core-shell copolymer (CS) film compared to conventional copolymer (CC) film.

Sample Code	T_g , °C	MFT, °C	Sample Code	T_g , °C	MFT, °C
CC1	41.8	40	CS1	42.2	≤30
CC2	44.4	45	CS2	43.2	30
CC3	44.8	50	CS3	44.1	30

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